REMARKS

Entry of this amendment and reconsideration of this application, as amended, is respectfully requested.

It is believed that the §112, second paragraph rejections do not apply to the newly presented claims.

Claims 1-8 were rejected under 35 U.S.C. §102(a) as allegedly obvious over the combination of Fritz et al. ("Fritz") in view of DE 4419816 (DE '816). Applicants respectfully traverse.

The Examiner acknowledges that Fritz, et al. (Fritz) fails to disclose blowing solid particles containing titanium into the slag.

DE '816 (copy of English translation enclosed) was cited for disclosing a titanium bearing slagging agent containing titania, silica, magnesia, calcia, iron oxide and alumina. Powder mixtures having a grain size of 50 to 5000 microns are disclosed. However, mean particle size d_{50} of from 0.001 to 1.0 mm does not appear to be disclosed. The advantages of such particle and means particle sizes are set forth in the specification, e.g., at page 5, line 23 to page 6.

If any additional fees are due to enter this amendment to maintain pendencey of this application, authorization is given to charge deposit account no: 50-0624.

Respectfully submitted,

FULBRIGHT & JAWORSKI L.L.P.

By _____
James R. Crawford
Reg. No. 39,155

666 Fifth Avenue
New York, NY 10103
212-318-3148

TRANSLATION: German Patent DE 44 19 816 C1

ADDITIVE CONTAINING TITANIUM AND ITS USE IN INCREASING THE DURABILITY OF THE REFRACTORY LINING OF A FURNACE AND AS A SLAG FORMER

The present invention describes a titaniferous additive consisting of residues from TiO_2 and one or more components selected from coal or coal-containing residues, iron, iron oxide, residues containing iron or iron oxide and one or more components selected from alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxide or alkaline metal hydroxide, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2. The present invention further describes a titaniferous additive, consisting of residues from TiO_2 production, one or more binding agents and one or more components selected from coal or coal-containing residues, iron, iron oxide, residues containing iron or iron oxide, and from one or more components selected from alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxide or alkaline earth metal hydroxide, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$, and SiO_2 or residues containing SiO_2, in the form of briquets, pellets or granules. The present invention lastly describes the use of additives containing titanium for increasing the durability of the refractory lining of an furnace and as a slag former.

DESCRIPTION

The present invention relates to an additive containing titanium and its use for increasing the durability of the refractory lining of an furnace and as a slag former.

As an additive for furnaces, especially blast furnaces, in the iron, steel and foundry industry, large amounts of natural ilmenite are used as a titanium source. Usually the natural ilmenite is crushed to a size of about 50 mm and fed directly into the furnace, The addition of ilmenite brings it about that the nitrogen content present in the raw iron is bound in the form of titanium nitrides and titanium carbonitrides. Thus the NOx reduction of the molten metal is achieved. By the partial depositing of the titanium compounds thus formed, on the inside walls of the refractory lining of the furnaces, especially in the superstructure of blast furnaces, the durability of the linings is increased. Natural ilmenite, however, must be obtained at great expense, while natural resources of high-quality ilmenite are diminished,

In DE 43 04 714 C1 ah additive containing titanium for furnaces is disclosed, consisting of residues from TiO_2 production and one or more components selected from coal or residues containing coal, iron, iron oxide, or residues containing iron or iron oxide.

In the iron, steel and foundry industries, additives are put into furnaces as slag formers. The additives are compounds occurring in nature and mixtures which contain, for example, the oxides CaO, Al_2O_3, SiO_2 and MgO. These additives must be purchased at great expense for their use as slag formers.

The purpose of the present invention is to offer, in an environmentally friendly and economical manner, an additive containing titanium as a substitute for the natural ilmenite used as an additive in metallurgical processes and as a replacement for the natural slag formers used as additives.

The problem at which the present invention is directed is solved by an additive containing titanium and consisting of residues from TiO_2 production and of one or more components selected from coal or residues containing coal, iron, iron oxide, residues containing iron or iron oxide and one or more components selected from alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxide or alkaline earth metal hydroxide, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3, or $Al(OH)_3$, and SiO_2 or residues containing SiO_2.

Residues from the production of titanium dioxide, especially titanium dioxide pigments, can be worked advantageously with residues containing coal, iron or iron oxides and with residues containing Al_2O_3, $Al(OH)_3$ or SiO_2. These residues are no longer dumped but are further processed economically pursuant to the invention.

The problem on which the present invention is based is further solved by an additive containing titanium, consisting of residues from TiO_2 production and one or more components selected from among alkaline earth metal oxides, alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2.

Residues from the production of titanium dioxide, especially titanium dioxide pigments, can advantageously be processed according to the invention with residues containing alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing Al_2O_3, $Al(OH)_3$ or SiO_2. These residues are no longer dumped, but are processed economically according to the invention.

A preferred embodiment of the invention is an additive containing titanium, consisting of 30 to 70 wt.-% of residues from TiO_2 production, 5 to 50 wt-% coal or residues containing coal and 20 to 65 wt-% of alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxides or alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3, $Al(OH)_3$, SiO_2 or residues containing SiO_2.

This composition according to the invention is well suited for the repair of thin refractory linings in furnaces. With this composition as a slag former, good results are also obtained

A preferred embodiment of the invention is an additive containing titanium, consisting of 30 to 70 wt-% of iron, iron oxide, residues containing iron or iron oxide and 20 to 65 wt-% of alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxides or alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3, or $Al(OH)_3$, or SiO_2 or residues containing SiO_2.

This composition according to the invention is especially suited for the repair of thin refractory linings in furnaces. Good results are also obtained with this composition as a slag

former.

A preferred embodiment of the invention is a titaniferous additive consisting of 50 to 95 wt-% of residues from TiO_2 production and 5 to 50 wt-% of alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxides or alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$, or SiO_2 or residues containing SiO_2.

This titaniferous additive according to the invention is well suited to the repair of thin refractory linings in furnaces. Very good results are obtained with this composition as a slag former. With CaO and residues containing CaO very good results are obtained in the adjustment of the basicity of slags. At the same time the binding of sulfur and phosphorus as sulfur and phosphorus compounds containing calcium is achieved to a great degree. By the addition of residues containing MgO and residues containing MgO, good results are additionally obtained in increasing the saturation in the slag that is formed. This prevents MgO contents from being dissolved out of the refractory lining. With residues containing Al_2O_3 or $Al(OH)_3$ as slag formers good results are obtained. These residues show very good results as fluxes for lime slags. In that case an acceleration of the dissolving of lime is achieved. With residues containing SiO_2 as slag formers very good results are obtained. In the case of the above-mentioned additive containing titanium, powder mixtures having a grain size of 50 to 5000 m are involved according to the invention.

A preferred embodiment of the invention is an additive containing titanium, which is in the form of sintered bodies. The sintered bodies are made by mixing the components, bringing the uniform mixture into sintering mold and then sintering it in a manner known in itself. The sintered material can be crushed to the desired size. The sintered bodies according to the invention show, in addition to good resistance to fracture, very good results as slag formers. With these sintered bodies good results are achieved in increasing the durability of the refractory lining of a furnace.

The problem that is the basis of the present invention is furthermore solved by an additive containing titanium, consisting of residues from the production ot TiO_2, one or more binding agents and one or more components selected from coal or residues containing coal, iron, iron oxide, residues containing iron or iron oxide, and one or more components selected from alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxide or alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and residues containing SiO_2 or residues containing SiO_2 in the form of briquets, pellets or granules. With this additive containing titanium very good results are obtained in regard to resistance to fracture. With this molded body according to the invention good results are obtained as a slag former and good results in improving the durability of the refractory lining of a furnace. The molded body according to the invention can be treated at temperatures of 100 C to 1000 C. The molded body configured as a briquette can be cylindrical, round, oval, rectangular or cubic.

The problem at the base of the present invention is furthermore solved by a titaniferous additive material consisting of residues from TiO_2 manufacture, one or more binding agents and one or more components chosen from alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxides or alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$, and SiO_2 or residues containing SiO_2. With this titaniferous additive very good results are obtained in regard to fracture resistance. These molded bodies according to the invention show very good results as slag formers and good results in improving the durability of the refractory lining of a furnace.

A preferred embodiment of the invention is a titaniferous additive containing 2 to 30 wt-% of binding agents. With this binding agent very good results are obtained regarding the fracture resistance of the molded bodies.

A preferred embodiment of the invention is a titaniferous additive wherein the binding agents are Portland cement, blast furnace cement, alumina cement or fly ash. According to the

invention, any available hydraulic, ceramic and chemical binding agent can be provided as binding agents as well as anti-swelling agents.

According to the invention, the use of a titaniferous additive as a powder mixture and/or in the form of molded bodies for loading into a furnace to increase the durability of the refractory lining of a furnace and as slag formers in the iron, steel and foundry industry.

The invention is further explained with the aid of an example.

Example

In a mixer the following were placed: 50 wt-% of the digestion residue from TiO_2 pigment manufacture by the sulfate process, containing 50 wt-% TiO_2, 23 wt-% Fe_2O_3, 6 wt-% CaO and 5 wt-% Fe_3O_3 as well as residue containing 12 wt-% CaO with a 95 wt-% CaO content (reckoned on the dry substance) and residue containing 18 wt-% MgO with a content of 89 wt-% MgO (reckoned on the dry substance). Then 13 wt-% of blast furnace cement containing 51 wt-% CaO, 27 wt-% SiO_2, 4.5 wt-% Al_2O_3, 4.5 wt-% TiO_2, 1.5 wt-% Fe_2O_3, 0.5 wt-% Mn_2 and 3.5 wt-% MgO as well as 1.5 wt-% of electrofilter ash containing 50 wt-% $SiO_{2,28}$ wt-% Al_2O_3, 7 wt-% Fe_2O_3, 3.2 wt-% CaO, 2.2 wt-% MgO, 3.8 wt-% K_2O and 0.9 wt-% Na_2O as well as 5.5 wt-% alumina cement containing 40 wt-% SiO_2, 25 wt-% Al_2O_3, 25 wt-%iO_2, 1.0 wt-% Fe_2O_3, 0.1wt-% Mn_2O_3 and 1.0 wt-% MgO were added and the mixture was intimately mixed. 50 Wt.-parts of this mixture were mixed with 50 wt.-parts of water. The aqueous mixture was homogenized for 2 minutes. The homogenous mixture was put into a briquette press . In the briquette press a pressure of 120 bar was established, at which cylindrical bodies (briquets) were obtained with an outside diameter of 80 mm and a length of 40 mm. After a curing time of 14 days, the briquets obtained had a fracture-resistance of 2950 N and a fracture-resistance of 3150 N after an hour and a half of heating at 1000 C in a 100% CO atmosphere. The cylindrical bodies (briquets) had the following composition:

Components	Content (wt.-%)
TiO_2	25.1
SiO_2	25.9
MgO	16.4
CaO	22.8
Al_2O_3	5.2
Fe_2O_2	2.5
Na	0.1
K	0.07
Residual components	1.93

To determine the durability (point strength) the bodies were subjected in a test press to a force acting on them with continuously increasing pressure until they broke. The force acting on the bodies upon fracture is taken as a measure of their durability.

Claims

1. Titaniferous additive, consisting of residues from TiO_2 production and one or more components, selected from coal or residues containing coal, iron, iron oxide or residues containing iron oxide, and one or more components selected from alkaline earth metal oxides, alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2.

2. Titaniferous additive, consisting of residues from TiO_2 production and one or more components selected from alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxides or alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2.

3. Titaniferous additive according to claim 1, consisting of 30 to 70 wt-% of residues from TiO_2 production, 5 to 50 wt-% of residues from TiO_2 production, 5 to 50 wt-% coal or residues containing coal and 20 to 65 wt-% of alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxides or alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$, SiO_2 or residues containing SiO_2.

4. Titaniferous additive according to claim 1, consisting of 30 to 70 wt-% of residues from TiO_2 production, 5 to 50 wt-% iron, iron oxide, residues containing iron or iron oxide, and 20 to 65 wt-% of alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxides or alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$ or residues containing Al_2O_3or $Al(OH)_3$, SiO_2 or residues containing SiO_2.

5. Titaniferous additive according to claim 2, consisting of 50 to 95 wt-% of residues from

TiO_2 production and 5 to 50 wt-% of alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxides or alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ residues, SiO_2 or residues containing SiO_2.

6. Titaniferous additive according to claims 1 to 5, in the form of sintered bodies.

7. Titaniferous additive, consisting of residues from TiO_2 production, one or more binding agents and one or more components selected from coal or residues containing coal, iron, iron oxide, residues containing iron or iron oxide and one or more components selected from alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxides or alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2 in the form of briquets, pellets or granules.

8. Titaniferous additive, consisting of residues from TiO_2 production, one or more binding agents and one or more components selected from alkaline earth metal oxides, alkaline earth metal hydroxides, residues containing alkaline earth metal oxides or alkaline earth metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2.

9. Titaniferous additive according to claims 7 and 8, containing 2 to 30 wt-% binding agent.

10. Titaniferous additive according to claims 7 to 9, wherein the binding agent is Portland cement, blast furnace cement, alumina cement or fly ash.

11. Use of a titaniferous additive as a powder mixture and/or in the form of molded bodies according to claims 1 to 10 for charging into a furnace to increase the durability of the refractory lining of a furnace and as slag former in the iron, steel and foundry industry.